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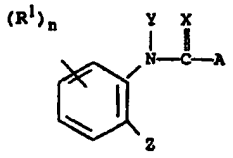
(54) Title: ANILIDE DERIVATIVES AS FUNGICIDES



(I)

(57) Abstract

Compounds of formula (I), wherein: X is O or S; A is a 6 membered heteroaryl group comprising at least one nitrogen atom, which is optionally substituted by one or more of the group R^2; R^1 is alkyl, cycloalkyl, cycloalkenyl, alkenyl, alkynyl or amino, (each of which is optionally substituted), Y^1-X-, halogen, cyano, nitro, acyl, acyloxy, optionally substituted heterocyclyl or optionally substituted phenyl; or two adjacent groups together with the carbon atoms to which they are attached can form an optionally substituted benzo ring; R^2 has the same meaning as R^1 or two adjacent groups together with the carbon atoms to which they are attached can form an optionally substituted heterocyclic ring; Y is alkyl, cycloalkyl, cycloalkenyl, alkenyl or alkynyl, each of which is optionally substituted, hydrogen or acyl; Y^1 has the same meaning as Y or is optionally substituted phenyl or optionally substituted heterocyclyl; Z is $C(=X^1)$-X^2-R^3, cyano, nitro, amino, acyl, optionally substituted heterocyclyl, $-C(R^5)=N-OR^6$ or $-C(R^5)=N-NR^6R^7$; R^3 is alkyl, cycloalkyl, cycloalkenyl, alkenyl, alkynyl, phenyl or heterocyclyl, each of which is optionally substituted, hydrogen or an inorganic or organic cationic group ; X^1 and X^2, which may be the same or different, are O or S , R^5, R^6 and R^7, which may be the same or different, are alkyl, cycloalkyl; cycloalkenyl, alkenyl, alkynyl, phenyl or heterocyclyl, each of which is optionally substituted or hydrogen or R^6 and R^7 together with the atom(s) to which they are attached can form a ring; n is 0 to 4, together with complexes with metal salts, as well as salts with bases of compounds which are acids and salts with acids of compounds which are bases, have fungidal activity.

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Title: ANILIDE DERIVATIVES AS FUNGICIDES

Field of the invention

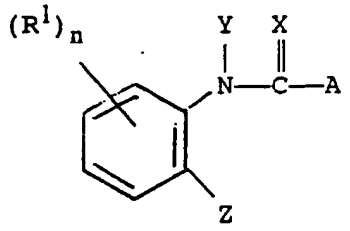
This invention relates to new derivatives of anthranilic acid useful as fungicides.

Prior Art

In GB 1,563,664 and Japanese Kokai 53130655, there are disclosed fungicidal esters of anthranilic acid. We have found that certain novel anthranilic acid derivatives also have valuable fungicidal activity and also have advantages over compounds disclosed in these publications.

Disclosure of the invention

According to the invention there is provided a compound of formula I



(I)

X is O or S;

A is a 6 membered heteroaryl group comprising at least one nitrogen atom, which is optionally substituted by one or more of the group R^2;

R^1 is alkyl, cycloalkyl, cycloalkenyl, alkenyl, alkynyl, or amino, (each of which is optionally substituted), Y^1-X-, halogen, cyano, nitro, acyl, acyloxy, optionally substituted heterocyclyl or optionally substituted phenyl; or two adjacent groups together with the carbon atoms to which they are attached can form an optionally substituted benzo ring;

R^2 has the same meaning as R^1 or two adjacent groups

together with the carbon atoms to which they are attached can form an optionally substituted heterocyclic ring;

Y is alkyl, cycloalkyl, cycloalkenyl, alkenyl or alkynyl, each of which is optionally substituted, hydrogen or acyl;

Y^1 has the same meaning as Y or is optionally substituted phenyl or optionally substituted heterocyclyl;

Z is $C(=X^1)-X^2-R^3$, cyano, nitro, amino, acyl, optionally substituted heterocyclyl, $-C(R^5)=N-OR^6$ or $-C(R^5)=N-NR^6R^7$;

R^3 is alkyl, cycloalkyl, cycloalkenyl, alkenyl, alkynyl, phenyl or heterocyclyl, each of which is optionally substituted, hydrogen or an inorganic or organic cationic group;

X^1 and X^2, which may be the same or different, are O or S;

R^5, R^6 and R^7, which may be the same or different, are alkyl, cycloalkyl, cycloalkenyl, alkenyl, alkynyl, phenyl or heterocyclyl, each of which is optionally substituted or hydrogen or R^6 and R^7 together with the atom(s) to which they are attached can form a ring;

and n is 0 to 4,

together with complexes with metal salts, as well as salts with bases of compounds which are acids and salts with acids of compounds which are bases, with the proviso that when Y is hydrogen and

i) when Z is carboxy, methoxycarbonyl or ethoxycarbonyl ring A is not unsubstituted pyridyl or pyrazinyl; and

ii) when Z is carboxy and n is 0, A is not 2-chloro-3-pyridyl, 6-(2-diethylaminoethoxy)-3-pyridyl or a 2-pyridyl group.

Alkyl groups are preferably of 1 to 20, eg 1 to 6, carbon atoms. Alkenyl and alkynyl groups are generally of 3 to 6 carbon atoms. Cycloalkyl or cycloalkenyl groups are

preferably of 3 to 8 carbon atoms.

Substituents, when present on any alkyl, cycloalkyl, cycloalkenyl, alkenyl or alkynyl moiety include halogen, azido, cyano, optionally substituted alkoxy, optionally substituted alkylthio, hydroxy, nitro, optionally substituted amino, acyl, acyloxy, optionally substituted phenyl, optionally substituted heterocyclyl, optionally substituted phenoxy and optionally substituted heterocyclyloxy.

Cycloalkyl or cycloalkenyl groups may also be substituted by alkyl.

Substituents when present on any phenyl group are usually one or more of the same groups as defined for R^1.

The term heterocyclyl includes both aromatic and non-aromatic heterocyclyl groups. Heterocyclyl groups are generally 5, 6 or 7-membered rings containing up to 4 hetero atoms selected from nitrogen, oxygen and sulfur. Examples of heterocyclyl groups are furyl, thienyl, pyrrolyl, pyrrolinyl, pyrrolidinyl, imidazolyl, dioxolanyl, oxazolyl, thiazolyl, imidazolyl, imidazolinyl, imidazolidinyl, pyrazolyl, pyrazolinyl, pyrazolidinyl, isoxazolyl, isothiazolyl, oxadiazolyl, triazolyl, thiadiazolyl, pyranyl, pyridyl, piperidinyl, dioxanyl, morpholino, dithianyl, thiomorpholino, pyridazinyl, pyrimidinyl, pyrazinyl, piperazinyl, triazinyl, thiazolinyl, benzimidazolyl, tetrazolyl, benzoxazolyl, imidazopyridinyl, 1,3-benzoxazinyl, 1,3-benzothiazinyl, oxazolopyridinyl, benzofuranyl, quinolinyl, quinazolinyl, quinoxalinyl, sulfolanyl, dihydroquinazolinyl, benzothiazolyl, phthalimido, benzofuranyl, azepinyl, oxazepinyl, thiazepinyl, diazepinyl and benzodiazepinyl.

Heterocyclyl groups may themselves be substituted for example as for phenyl.

Amino groups may be substituted for example by one or two optionally substituted alkyl or acyl, or two substituents can form a ring, preferably a 5 to 7-membered ring, which may be substituted and may contain other heteroatoms, for example morpholine, thiomorpholine, or piperidine.

The term acyl includes the residue of sulfur and phosphorus-containing acids as well as carboxylic acids. Examples of acyl groups are thus $-COR^5$, $-COOR^5$, $-CXNR^5R^6$, $-CON(R^5)OR^6$, $-COONR^5R^6$, $-CON(R^5)NR^6R^7$, $-COSR^5$, $-CSSR^5$, $-S(O)_pR^5$, $-S(O)_2OR^5$, $-S(O)_pNR^5R^6$, $-P(=X)(OR^5)(OR^6)$, $-CO-COOR^5$, where R^5, R^6 and R^7 are as defined previously, or R^6 and R^7 together with the atom(s) to which they are attached can form a ring, p is 1 or 2 and X is O or S.

It is generally preferred that A is a pyridine, (especially 3-pyridyl), a pyrimidine (especially 5-pyrimidinyl), or a pyrazine ring. A may also be for example a tetrazine, pyridazine or triazine ring.

R^2 is preferably selected from halogen and alkoxy, especially methoxy.

R^1 is preferably selected from halogen, especially fluorine, and alkyl, especially methyl.

Z is preferably $C(=X^1)-X^2-R^3$. X^1 and X^2 are both preferably O and R^3 is generally alkyl, alkenyl or alkynyl, each of which is optionally substituted, and is especially methyl.

Y is preferably hydrogen, alkyl, especially methyl or acyl, especially alkanoyl or alkoxycarbonyl.

X is preferably O.

n is preferably 0.

Complexes of compounds of the invention are usually formed from a salt of formula MAn_2, in which M is a divalent metal cation, e.g. copper, manganese, cobalt, nickel, iron or zinc and An is an anion, e.g. chloride, nitrate or sulfate.

The compounds of the invention have activity against a wide range of pathogens of Deuteromycete, Ascomycete, Phycomycete and Basidiomycete origin, especially against fungal diseases of plants, e.g. mildews and particularly barley powdery mildew (*Erysiphe graminis*) cucumber powdery mildew (*Erysiphe cichoracaerum*) and vine downy mildews (*Plasmopara viticola* and *Uncinula necator*), rice blast (*Pyricularia oryzae*), cereal eyespot (*Pseudocercosporella herpotrichoides*), rice sheath blight (*Pellicularia sasakii*), grey mould (*Botrytis cinerea*), wheat brown rust (*Puccinia recondita*), late tomato or potato blight (*Phytophthora infestans*), apple scab (*Venturia inaequalis*) and glume blotch (*Leptosphaeria nodorum*). Some compounds may be active against only a few pathogens whereas others may have a broader spectrum of activity.

Some novel compounds of formula I have weak pesticidal activity but still have utility as intermediates and such compounds also form one aspect of the invention.

The compounds of the invention are generally formulated in conventional compositions used for fungicides. These compositions can contain one or more additional pesticides, for example compounds known to possess herbicidal, fungicidal, insecticidal, acaricidal or

nematicidal properties.

The diluent or carrier in the composition of the invention can be a solid or a liquid optionally in association with a surface-active agent, for example a dispersing agent, emulsifying agent or wetting agent. Suitable surface-active agents include anionic compounds such as a carboxylate, for example a metal carboxylate of a long chain fatty acid; an N-acylsarcosinate; mono- or di-esters of phosphoric acid with fatty alcohol ethoxylates or salts of such esters; fatty alcohol sulfates such as sodium dodecyl sulfate, sodium octadecyl sulfate or sodium cetyl sulfate; ethoxylated fatty alcohol sulfates; ethoxylated alkylphenol sulfates; lignin sulfonates; petroleum sulfonates; alkyl-aryl sulfonates such as alkyl-benzene sulfonates or lower alkylnaphthalene sulfonates, e.g. butyl-naphthalene sulfonate; salts of sulfonated naphthalene-formaldehyde condensates; salts of sulfonated phenol-formaldehyde condensates; or more complex sulfonates such as the amide sulfonates, e.g. the sulfonated condensation product of oleic acid and N-methyl taurine or the dialkyl sulfosuccinates, e.g. the sodium sulfonate of dioctyl succinate. Nonionic agents include condensation products of fatty acid esters, fatty alcohols, fatty acid amides or fatty-alkyl- or alkenyl-substituted phenols with ethylene oxide, fatty esters of polyhydric alcohol ethers, e.g. sorbitan fatty acid esters, condensation products of such esters with ethylene oxide, e.g. polyoxyethylene sorbitan fatty acid esters, block copolymers of ethylene oxide and propylene oxide, acetylenic glycols such as 2,4,7,9-tetramethyl-5-decyne-4,7-diol, or ethoxylated acetylenic glycols. Examples of a cationic surface-active agent include, for instance, an aliphatic mono-, di-, or polyamine as an acetate, naphthenate or oleate; an oxygen-containing amine such as an amine oxide or polyoxyethylene alkylamine; an

amide-linked amine prepared by the condensation of a carboxylic acid with a di- or polyamine; or a quaternary ammonium salt.

The compositions of the invention can take any form known in the art for the formulation of agrochemicals, for example, a solution, a dispersion, an aqueous emulsion, a dusting powder, a seed dressing, a fumigant, a smoke, a dispersible powder, an emulsifiable concentrate or granules. Moreover it can be in a suitable form for direct application or as a concentrate or primary composition which requires dilution with a suitable quantity of water or other diluent before application.

As a dispersion, the composition comprises a compound of the invention dispersed in a liquid medium, preferably water. It is often convenient to supply the consumer with a primary composition which can be diluted with water to form a dispersion having the desired concentration. The primary composition can be provided in any one of the following forms. It can be a dispersible solution which comprises a compound of the invention dissolved in a water-miscible solvent with the addition of a dispersing agent. A further alternative comprises a compound of the invention in the form of a finely ground powder in association with a dispersing agent and intimately mixed with water to give a paste or cream which can if desired be added to an emulsion of oil in water to give a dispersion of active ingredient in an aqueous oil emulsion.

An emulsifiable concentrate comprises a compound of the invention dissolved in a water-immiscible solvent together with an emulsifying agent and which is formed into an emulsion on mixing with water.

A dusting powder comprises a compound of the invention intimately mixed with a solid pulverulent diluent, for example, kaolin.

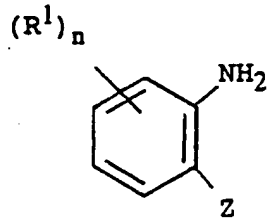
A granular solid comprises a compound of the invention associated with similar diluents to those which may be employed in dusting powders, but the mixture is granulated by known methods. Alternatively it comprises the active ingredient adsorbed or absorbed on a pre-granular diluent, for example, Fuller's earth, attapulgite or limestone grit.

A wettable powder usually comprises the active ingredient in admixture with a suitable surfactant and an inert powder diluent such as china clay.

Another suitable concentrate, particularly when the product is a solid, is a flowable suspension concentrate which is formed by grinding the compound with water, a wetting agent and a suspending agent.

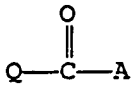
The concentration of the active ingredient in the composition of the present invention is preferably within the range of 1 to 30 per cent by weight, especially 5 to 30 per cent by weight. In a primary composition the amount of active ingredient can vary widely and can be, for example, from 5 to 95 per cent by weight of the composition.

The compounds of the invention may be prepared in known manner, for example by reacting a compound of formula II,



(II)

with a compound of formula III



(III)

where Q is a leaving group, preferably a halogen and especially chlorine, to give a compound of formula I, where X is O and Y is hydrogen, and if desired modifying this compound in known manner to give other compounds where X and/or Y have other desired values, and if desired modifying compounds of formula I in known manner to give compounds where R^1, R^2 and Z have other values.

The reaction between compounds II and III is generally carried out in the presence of a base, e.g. an organic tertiary amine and preferably in the presence of a solvent, e.g. an ether.

The compounds of formula II and III are either known or can be prepared in known manner.

The resulting compounds of formula I may be modified in known manner to give other compounds of formula I where one of the groups are modified to other desired groups.

For example an ester may be converted in known manner to a free acid or a salt.

Thio groups may be oxidised using a suitable oxidising agent, eg m-chloroperbenzoic acid, to give sulfinyl and sulfonyl groups.

Carbonyl groups may be converted to thiocarbonyl groups by sulfurising in known manner, e.g. using Lawesson's reagent or phosphorus pentasulfide.

Alkylsulfonyl groups on ring A may be replaced by a suitable nucleophile such as an aryloxy or arylthio group by reaction with the appropriate hydroxy or mercapto compound.

The invention is illustrated in the following Examples. Structures of isolated novel compounds were confirmed by elemental and/or other appropriate analyses. Temperatures are in °C.

Example 1

Triethylamine (28.4 g) was added to a solution of 6-chloronicotinic acid (40 g) in dry dichloromethane (900 ml). The mixture was cooled in an ice bath and methyl chloroformate (26.8 g) was added dropwise. The mixture was stirred at room temperature overnight, washed in turn with water, aqueous sodium hydrogen carbonate and brine. The organic phase was dried over magnesium sulfate, filtered and evaporated to give methyl 6-chloronicotinate.

10 g of this product was added to sodium methanolate (obtained from 1.61 g sodium and 100 ml dried methanol). The mixture was heated under reflux for 3 hours and allowed to stand at room temperature overnight. Aqueous potassium hydroxide (10 g in 30 ml water) was added and the mixture was heated under reflux for 8 hours. It was left to stand overnight at room temperature, evaporated and the residue added to water (120 ml). The mixture was acidified to pH 3 with hydrochloric acid. The precipitate was filtered and dried to give 6-methoxynicotinic acid, m.p. 175-177°.

This acid (6 g) was heated under reflux with an excess amount of thionyl chloride for 2 hours. The mixture was cooled, evaporated and the residue (comprising crude 6-methoxynicotinoyl chloride) was dissolved in dry tetrahydrofuran (10 ml). This solution was added dropwise to a solution of methyl anthranilate (6.22 g) and triethylamine (7.92 g) in dry tetrahydrofuran (200 ml). The mixture was stirred at room temperature overnight, evaporated and extracted with ethyl acetate. The extracts were washed with water, dried and evaporated and the residue purified by silica gel column chromatography to give methyl N-(6-methoxynicotinoyl)anthranilate, m.p. 121-3°. (compound 1)

In a similar manner there was obtained methyl N-(2-methylthio-5-pyrimidinecarbonyl)anthranilate, m.p. 166-8°. (compound 1a)

Example 2

Sodium hydride (0.15 g of a 60% solution in oil) was added to a solution of the compound 1 from Example 1 (1 g) in dry tetrahydrofuran (25 ml) which had been cooled on an ice bath. The mixture was stirred for 20 minutes and then methyl iodide (0.44 ml) was added. The mixture was stirred at room temperature for 48 hours, evaporated and extracted with ethyl acetate. The extract was washed in turn with water and brine, dried over magnesium sulfate and evaporated. The residue was purified by silica gel column chromatography to give methyl N-(6-methoxynicotinoyl)-N-methylanthranilate), m.p. 68-70°. (compound 2)

Example 3

To a solution of compound 2 from Example 2 (0.6 g) in ethanol (20 ml) was added copper(II)chloride (0.134 g). The mixture was allowed to stand overnight, evaporated and the residue triturated with ethyl acetate to give

bis-[methyl N-(6-methoxynicotinoyl)-N-methylanthranilate] copper(II)chloride complex, m.p. 196-8°. (compound 3)

Example 4

m-Chloroperbenzoic acid (13.7 g) was added with stirring to a solution of compound 1a (6 g) in dichloromethane. The mixture was stirred overnight at room temperature, sodium sulfate added and extracted with dichloromethane. The extract was worked up to give methyl N-(2-methylsulfonyl-5-pyrimidinecarbonyl)anthranilate, m.p. 187-9°. (compound 4)

Example 5

Sodium hydride (0.24 g of a 60% dispersion in oil) was added to a solution of 2-mercaptopyridine (0.33 g) dissolved in dry dimethylformamide (20 ml). The mixture was stirred for half an hour at room temperature. A solution of compound 4 (1 g) in dry dimethylformamide (20 ml) was added dropwise with stirring. The mixture was stirred overnight at room temperature. It was cooled and quenched with methanol. The mixture was poured into water and made acidic with dilute hydrochloric acid. The precipitate was collected, dissolved in dichloromethane and the solution washed with brine and evaporated to give methyl N-[2-(2-pyridylthio)-5-pyrimidinecarbonyl]-anthranilate, mp. 145-147° (compound 5)

In a similar manner using potassium carbonate as the base instead of sodium hydride there was obtained methyl N-[2-(4-methoxyphenoxy)-5-pyrimidinecarbonyl]-anthranilate, as an oil (compound 5a).

Example 6

Compound 1 was heated with an equimolar amount of aqueous sodium hydroxide to give N-(6-methoxynicotinoyl)-anthranilic acid m.p. 224-3° (compound 6).

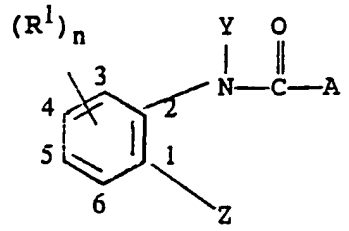
This compound in turn was treated with further sodium hydroxide to give sodium N-(6-methoxynicotinoyl)-anthranilate, m.p. >250° (compound 6a).

Example 7

Lawesson's reagent (2,4-bis(4-methoxyphenyl)-1,3-dithia-2,4-diphosphetane 2,4-disulfide; 5.09 g) was added to a solution of compound 1 (3 g) in dry tetrahydrofuran (100 ml). The mixture was stirred under nitrogen for 20 hours. More Lawesson's reagent (2,6 g) was added and the mixture heated under reflux for 13 hours, evaporated and the residue purified by silica gel column chromatography to give methyl N-(6-methoxy-3-pyridinethiocarbonyl)-anthranilate, m.p. 133-4°. (compound 7)

Example 8

In a similar manner to one of the processes disclosed in t he previous Examples, the following compounds of formula I were obtained.



(I)

Cpd	$(R^1)_n$	Z	Y	A	m.p.(°)
8	-	COOMe	H	6-EtO-3-pyridyl	150-2
9	-	COOEt	H	6-MeO-3-pyridyl	129-30
10	-	COOEt	Me	6-MeO-3-pyridyl	91-2
11	-	COOMe	$-CH_2CN$	6-MeO-3-pyridyl	oil
12	-	COOMe	-COOMe	6-MeO-3-pyridyl	gum
13	3-Me	COOMe	H	6-MeO-3-pyridyl	111-2
14	5-Cl	COOMe	H	6-MeO-3-pyridyl	172-3
15	4,5-$(MeO)_2$	COOMe	H	6-MeO-3-pyridyl	173-5
16	-	COObenzyl	Me	6-MeO-3-pyridyl	110-3
17	5-Cl	COOMe	Me	6-MeO-3-pyridyl	89-91
18	4,5-$(MeO)_2$	COOMe	Me	6-MeO-3-pyridyl	147-50
19	5-MeS	COOMe	H	6-MeO-3-pyridyl	135-7
20	5-MeS	COOMe	Me	6-MeO-3-pyridyl	78-80
21	-	CN	H	6-MeO-3-pyridyl	163-6
22	-	CN	Me	6-MeO-3-pyridyl	90.5-3
23	-	COMe	H	6-MeO-3-pyridyl	131.5-4
24	-	NO_2	H	6-MeO-3-pyridyl	125-7
25	-	COOMe	H	5-MeO-2-pyrazinyl	169-70
26	6-Me	COOMe	H	6-MeO-3-pyridyl	102.5-5
27	-	COOMe	H	5-Cl-6-MeO-3-pyridyl	165-6

Cpd	$(R^1)_n$	Z	Y	A	m.p.(°)
28	-	COOMe	Me	5-Cl-6-MeO-3-pyridyl	110-2
29	6-Me	COOMe	Me	6-MeO-3-pyridyl	117.5-8.5
30	-	$COOPr_i$	H	6-MeO-3-pyridyl	107-9
31	-	COOMe	H	6-MeS-3-pyridyl	102.5-5
32	-	COOMe	Me	6-EtO-3-pyridyl	oil
33	-	COOMe	H	4,6-$(MeO)_2$-5-pyrimidinyl	125-7
34	-	COOMe	H	5,6-$(MeO)_2$-2-pyrazinyl	156-9
35	-	COOMe	Me	3-pyridyl	86-8
36	-	SO_2Me	H	6-MeO-3-pyridyl	148.5-50.5
37	-	SOMe	H	6-MeO-3-pyridyl	111-3
38	4-NO_2	COOMe	Me	6-MeO-3-pyridyl	110-2
39	-	COOH	2-F-benzyl	6-MeO-3-pyridyl	195-7
40	4-MeOCO	COOMe	Me	6-MeO-3-pyridyl	109-12
41	-	CONH-OMe	H	6-MeO-3-pyridyl	152-3
42	-	COOMe	H	5-(3-thienyl)-3-pyridyl	149-50
43	-	COOMe	Me	6-NH_2-3-pyridyl	119-22
44	-	COOMe	H	6-Pr^iO-3-pyridyl	15-7
45	-	tetrazol-5-yl	Me	6-MeO-3-pyridyl	198-200
46	-	SO_2Me	Me	6-MeO-3-pyridyl	100-2
47	-	COOMe	H	6-MeCOO-3-pyridyl	109-12
48	3-Cl	COOMe	H	6-MeO-3-pyridyl	106-10
49	-	COOMe	H	4-Cl-2-pyridyl	158-60
50	-	COOPr	H	6-MeO-3-pyridyl	107-9
51	-	COOBu	H	6-MeO-3-pyridyl	57-60
52	-	COOPr	Me	6-MeO-3-pyridyl	81.5-4
53	-	COOBu	Me	6-MeO-3-pyridyl	72-6
54	3-Cl	COOMe	Me	6-MeO-3-pyridyl	84-7

Cpd	$(R^1)_n$	Z	Y	A	m.p.(°)
55	-	CON(Me)-OMe	Me	6-MeO-3-pyridyl	147-50
56	-	CHO	H	6-MeO-3-pyridyl	117-20
57	-	COO-allyl	H	6-MeO-3-pyridyl	98-9.5
58	4-Cl	COOMe	Me	6-MeO-3-pyridyl	98-100
59	-	COOMe	$-CH_2C\equiv CH$	6-MeO-3-pyridyl	84.5-87
60	-	C(Me)=N-NHMe	H	6-MeO-3-pyridyl	124-34
61	-	C(Me)=N-OMe	H	6-MeO-3-pyridyl	115-6
62	4-F	COOMe	H	6-MeO-3-pyridyl	125-6
63	-	$COONH_4$	H	6-MeO-3-pyridyl	250-2
64	5,6-benzo	COOMe	H	6-MeO-3-pyridyl	157-61
65	$4-CF_3$	COOMe	H	6-MeO-3-pyridyl	139-42
66	-	COOMe	$4-CF_3$-benzyl	6-MeO-3-pyridyl	111-3
67	-	CON(Me)-OMe	H	6-MeO-3-pyridyl	102-4
68	-	COOMe	H	6-MeNH-3-pyridyl	187-89
69	-	COOMe	2-Me-benzyl	6-MeO-3-pyridyl	112-4
70	-	COOMe	4-MeO-benzyl	6-MeO-3-pyridyl	119-21
71	-	CONH(CH_2Ph)	H	6-MeO-3-pyridyl	165-7
72	-	COOMe	Me	2-pyridyl	80-2
73	-	COOMe	H	2-MeO-4-pyridyl	132-5
74	-	COOMe	H	$5,6-Cl_2$-3-pyridyl	161-2
75	-	$COO^- N^+Bu_4$	H	6-MeO-3-pyridyl	250-2
76	-	COOMe	H	2-Cl-3-pyridyl	120-1
77	-	COOMe	H	2-MeO-3-pyridyl	78-81

Cpd	$(R^1)_n$	Z	Y	A	m.p.(°)
78	-	CHO	Me	6-MeO-3-pyridyl	83-4
79	-	CH=N-OH	H	6-MeO-3-pyridyl	145-6
80	-	C(=N-NMe_2)Me	H	6-MeO-3-pyridyl	87-9
81	-	I	H	6-MeO-3-pyridyl	140-2
82	-	COOMe	H	2-MeS-3-pyridyl	117-9
83	-	COOMe	H	5-Br-6-MeO-3-pyridyl	164-5
84	-	COOMe	Me	5-Br-6-MeO-3-pyridyl	112-4
85	-	COOMe	H	5-MeO-2-pyridyl	141-3
86	-	COOMe	H	6-Me-3-pyridyl	125-6
87	5-Me	COOMe	H	2-MeO-3-pyridyl	139-40
88	-	$COOC_5H_{11}$	H	6-MeO-3-pyridyl	49-52
89	-	$COOCH_2$-COOMe	H	6-MeO-3-pyridyl	125-7
90	-	$COOCH_2$-C≡CH	H	6-MeO-3-pyridyl	129-32
91	-	$COOBu^i$	H	6-MeO-3-pyridyl	81-3
92	-	COOMe	H	5-Ph-6-MeO-3-pyridyl	159-61
93	-	COOMe	$-CH_2COOMe$	6-MeO-3-pyridyl	oil
94	-	COObenzyl	H	2-MeO-3-pyridyl	79-80
95	-	CONHMe	H	6-MeO-3-pyridyl	162-4
96	-	C(=N-OMe)Me	Me	6-MeO-3-pyridyl	oil
97	-	Ph	H	6-MeO-3-pyridyl	107-9
98	-	5-(4-Cl-Ph)-1,3,4-oxadiazol-2-yl	H	6-MeO-3-pyridyl	193-7

Cpd	$(R^1)_n$	Z	Y	A	m.p.(°)
99	-	$COO^- \overset{\text{cyclohexyl}}{\underset{\text{cyclohexyl}}{N^+H_2}}$	H	6-MeO-3-pyridyl	203-5
100	4-F,5-Me	COOMe	H	2-MeO-3-pyridyl	glass
101	-	2-furyl	H	6-MeO-3-pyridyl	112-7
102	-	$COOCH_2$-CH_2Cl	H	6-MeO-3-pyridyl	155-8
103	-	COOMe	Me	2-MeO-3-pyridyl	oil
104	5-F	COOMe	H	6-MeO-3-pyridyl	125-6
105	-	COOMe	allyl	6-MeO-3-pyridyl	oil
106	-	COOMe	acetyl	6-MeO-3-pyridyl	oil
107	-	COOMe	benzoyl	6-MeO-3-pyridyl	117-8
108	-	COOMe	3,4-MeO_2-Ph-CH_2CH_2-	6-MeO-3-pyridyl	116-8
109	-	COOMe	H	5-MeO-3-pyridyl	117-9
110	-	COOMe	-CH_2Ph	5-Cl-6-MeO-3-pyridyl	126-8
111	-	COOMe	Me	5,6-Cl_2-3-pyridyl	103-4
112	-	COOMe	H	5-Cl-6-MeS-3-pyridyl	167-9
113	-	COOMe	H	5-Br-3-pyridyl	122-3
114	-	5-(4-Cl-Ph)-1,3,4-oxadiazol-2-yl	Me	6-MeO-3-pyridyl	188-91
115	-	COOMe	Me	4,6-$(MeO)_2$-2-pyrimidinyl	111-3
116	4-Me	COOMe	H	6-MeO-3-pyridyl	116-9
117	-	COOMe	Me	5-MeO-2-pyridyl	82-4
118	-	SO_2NHMe	H	6-MeO-3-pyridyl	solid
119	5-Me	COOMe	H	6-MeO-3-pyridyl	160-2
120	-	COOMe	Me	5-MeO-3-pyridyl	60-2
121	6-Cl	COOMe	H	6-MeO-3-pyridyl	160-2

Cpd	$(R^1)_n$	Z	Y	A	m.p.(°)
122	-	COOMe	H	5,6-$(MeO)_2$-3-pyridyl	155-7
123	-	5-(4-Cl-Ph)-1,3,4-thiadiazol-2-yl	H	6-MeO-3-pyridyl	215-7
124	-	CONH(COOMe)	H	6-MeO-3-pyridyl	140-2
125	4-Cl	COOMe	H	2-($MeSO_2$)-5-pyrimidinyl	183-5
126	5-NO_2	COOMe	H	6-MeO-3-pyridyl	197-9
127	3,5-Me_2	COOMe	H	6-MeO-3-pyridyl	131-3
128	-	COOMe	SO_2Me	6-MeO-3-pyridyl	125-8
129	-	COOMe	H	4-MeO-2-$MeSO_2$-5-pyrimidinyl	187-90
130	-	1-pyrrolyl	H	6-MeO-3-pyridyl	113-6
131	4-Cl	COOMe	H	2-MeO-5-pyrimidinyl	175-7
132	6-F	COOMe	H	6-MeO-3-pyridyl	177-9
133	4-MeO	COOMe	H	6-MeO-3-pyridyl	164-5
134	-	COOMe	-CH(Me)Ph	6-MeO-3-pyridyl	132-3
135	-	COOMe	Me	5,6-$(MeO)_2$-3-pyridyl	110-2
136	-	$COCH_2OMe$	H	6-MeO-3-pyridyl	110-2
137	-	$CONH_2$	H	6-MeO-3-pyridyl	224-8
138	-	COOMe	H	4-Cl-6-[N-(2-MeOCO-Ph)NHCO]-2-pyridyl	210-2
139	-	COOMe	H	4-MeO-6-[N-(2-MeO-CO-Ph)NHCO]-2-pyridyl	195-9
140	-	COOMe	H	6-[N-(2-MeOCO-Ph)-NHCO]-3-pyridyl	198-200
141	-	COOMe	H	6-CF_3CH_2O-3-pyridyl	173-4

Cpd	$(R^1)_n$	Z	Y	A	m.p.(°)
142	-	COOMe	H	2,5-$(MeO)_2$-6-[N-(2-MeOCO-Ph)NHCO]-3-pyridyl	195-9
143	-	COOMe	H	4,6-$(EtO)_2$-2-pyridyl	115-6
144	-	$CONEt_2$	H	6-MeO-3-pyridyl	oil
145	-	$CONHNH_2$	H	6-MeO-3-pyridyl	188-9
146	-	CONH-N=CMe_2	H	6-MeO-3-pyridyl	174-7
147	-	COOMe	2-Me-benzyl	2-MeO-3-pyridyl	101-3
148	5-NH_2	COOMe	H	6-MeO-3-pyridyl	171-3
149	-	COOMe	H	6-(2,3,4-Cl_3-1-pyrrolyl)-3-pyridyl	183
150	-	SCH_2CH_2CN ‖ O	H	6-MeO-3-pyridyl	113-5
151	-	2-benzimidazolyl	H	6-MeO-3-pyridyl	272-5
152	-	O ‖ SCH_2CH_2CN ‖ O	H	6-MeO-3-pyridyl	141-3
153	-	CONHNH-COMe	H	6-MeO-3-pyridyl	193-7
154	-	COO-allyl	H	5-Cl-6-MeO-3-pyridyl	113-5
155	-	$COOCH_2$-C≡CH	H	5-Cl-6-MeO-3-pyridyl	163-5
156	3-F	COOMe	H	6-MeO-3-pyridyl	107-9
157	5-OH	COOMe	H	6-MeO-3-pyridyl	203-5
158	5-I	COOMe	H	6-MeO-3-pyridyl	154-6
159	5-MeOCO	COOMe	H	6-MeO-3-pyridyl	155-6

Cpd	$(R^1)_n$	Z	Y	A	m.p.(°)
160	5-MeCONH	COOMe	H	6-MeO-3-pyridyl	253-6
161	-	COOMe	-CH(Me)-COOMe	6-MeO-3-pyridyl	134-5
162	-	COOMe	2-Me-benzyl	5-Cl-6-MeO-3-pyridyl	oil
163	-	COOEt	H	5-Cl-6-MeO-3-pyridyl	136-8
164	-	COOH	H	5-Cl-6-MeO-3-pyridyl	247-50
165	5-$MeSO_2NH$	COOMe	H	6-MeO-3-pyridyl	184-5
166	-	COOMe	H	5-cyano-3-pyridyl	190-2
167	-	COOMe	H	6-formyl-3-pyridyl	153-7
168	-	CONH-(4-Cl-Ph)	H	6-MeO-3-pyridyl	188-90
169	-	COOMe	H	5-Br-2-MeO-3-pyridyl	180-2
170	4-Cl	COOMe	Me	2-MeO-5-pyrimidinyl	86-8
171	-	COOMe	H	2-Cl-4-pyridyl	108-10
172	-	COOMe	H	2-Cl-6-MeO-3-pyridyl	144-5
173	-	COOMe	H	6-(2,3,4,5-Cl_4-1-pyrrolyl)-3-pyridyl	289
174	-	COONa	H	6-Cl-3-pyridyl	300
175	-	COOMe	H	6-$MeOCH_2$-3-pyridyl	117-8
176	-	COOMe	H	5-cyano-6-MeO-3-pyridyl	247-50
177	-	5-Me-1,3,4-thiadiazol-2-yl	H	6-MeO-3-pyridyl	143-5
178	-	COOMe	H	5-cyano-6-Me_2N-3-pyridyl	190-2
179	-	COOMe	H	5-$MeSO_2O$-3-pyridyl	149-51

Cpd	$(R^1)_n$	Z	Y	A	m.p.(°)
180	-	COOMe	H	6-(2,3,5-Cl_3-1-pyrrolyl)-3-pyridyl	134-5
181	-	COOMe	H	6-MeOCO-3-pyridyl	141
182	-	COOMe	H	5-$PhCH_2O$-3-pyridyl	123-31
183	-	COOMe	H	5-MeS-3-pyridyl	122-3
184	-	COOMe	H	5-MeOCO-2-pyridyl	187-8
185	-	COOMe	H	2,6-$(MeO)_2$-3-pyridyl	141-3
186	-	COOMe	H	5-$MeSO_2$-3-pyridyl	168-70
187	-	COOMe	H	5-MeSO-3-pyridyl	130-2
188	-	COOMe	Me	5-MeS-3-pyridyl	oil
189	-	COOMe	H	5-(N≡C-CH_2O)-3-pyridyl	solid
190	-	COOMe	Me	5-$MeSO_2$-3-pyridyl	109-11
191	-	COOMe	H	5-$ClCH_2S$-3-pyridyl	112-4
192	-	COOH	H	6-Cl-3-pyridyl	240
193	-	COOMe	H	5-MeOCO-3-pyridyl	147-8
194	-	COOMe	H	6-[N-(2-MeOCO-Ph)-NHCO]-3-pyridyl	195-9
195	-	COOMe	H	5-Me-3-pyridyl	116-7
196	-	COOMe	H	6-MeO-5-NO_2-3-pyridyl	150-1
197	-	COOMe	H	6-PhO-3-pyridyl	97-8
198	-	COOMe	H	5,6-$(MeS)_2$-3-pyridyl	157-8
199	-	-CO-COOMe	H	6-MeO-3-pyridyl	133-6
200	-	COOMe	Me	2,6-$(MeO)_2$-3-pyridyl	103-5
201	-	COOMe	Me	5-MeOCO-3-pyridyl	oil
202	-	COOMe	Me	5-Me-3-pyridyl	114-5
203	-	COOH	H	5-HOCO-3-pyridyl	275

Cpd	$(R^1)_n$	Z	Y	A	m.p.(°)
204	-	COOMe	H	5-acetyl-6-Me-3-pyridyl	144-5
205	-	COOMe	H	5-Ph-3-pyridyl	124-5
206	-	COOMe	Me	6-PhO-3-pyridyl	114-5
207	-	COOMe	H	5-[N-(2-MeOCO-Ph)-NHCO]-3-pyridylthio	180-2
208	-	COOMe	H	5-$PhCH_2S$-3-pyridyl	104-6
209	-	COOMe	Me	5-MeO-2-pyrazinyl	81-3
210	4-F	COOMe	Me	6-MeO-3-pyridyl	102-4
211	-	COOMe	Et	6-MeO-3-pyridyl	53-5
212	-	COOMe	H	2-MeO-5-pyrimidinyl	164-5
213	-	COOMe	Me	2-MeO-5-pyrimidinyl	128-30
214	-	COOMe	H	4,6-$(MeO)_2$-2-$PhCH_2O$-5-pyrimidinyl	127-9
215	-	COOMe	H	2-Cl-4CF_3-5-pyrimidinyl	139-40
216	-	COOMe	H	2-Me_2N-4CF_3-5-pyrimidinyl	133-6
217	-	COOMe	H	2-MeO-4CF_3-5-pyrimidinyl	13940
218	-	COOMe	H	6-Cl-5-MeO-2-pyrazinyl	168-71
219	-	COOMe	H	5-Br-2-Me-4-pyrimidinyl	165-6
220	-	COOMe	H	2,4,6-$(MeO)_3$-5-pyrimidinyl	153-5
221	-	COOMe	Me	6-Cl-3-pyridyl	84-6
222	-	COOMe	H	2-Cl-4-pyrimidinyl	159-61
223	-	COOMe	H	5-Me-2-pyrazinyl	158-60.5
224	-	COOMe	H	2-MeO-4-pyrimidinyl	135-6
225	-	COOPr	H	2-$MeSO_2$-5-pyrimidinyl	129-31

Cpd	$(R^1)_n$	Z	Y	A	m.p.(°)
226	-	COOPr	H	2-MeSO-5-pyrimidinyl	116-8
227	-	COOPr	H	2-MeO-5-pyrimidinyl	104-5
228	-	COOEt	H	2-EtO-5-pyrimidinyl	134-5
229	-	COOH	H	2-EtO-5-pyrimidinyl	150-62
230	-	COOMe	H	2-Me-5-pyrimidinyl	141-3
231	-	COOMe	H	5-pyrimidinyl	158-61
232	-	COOMe	Me	2-Me-5-pyrimidinyl	88-90
233	-	COOMe	H	2-Cl-5-pyrimidinyl	159-61
234	-	COOMe	H	2-Br-5-pyrimidinyl	177-8
235	-	COOMe	H	2-$PhCH_2NH$-5-pyrimidinyl	192-4
236	-	COOMe	H	2-morpholino-5-pyrimidinyl	222-3
237	-	COOMe	H	5-Br-2-MeS-4-pyrimidinyl	192-4
238	-	COOMe	H	5-Br-2-MeO-4-pyrimidinyl	178-80
239	-	COOMe	H	2-$MeOCOCH_2NH$-5-pyrimidinyl	194-7
240	-	COOMe	H	2,6-Cl_2-4-pyrimidinyl	170-5
241	-	COOMe	H	2-CF_3-5-pyrimidinyl	143-5
242	-	COOMe	H	2-Ph-5-pyrimidinyl	151-5
243	-	COOMe	H	2,6-$(MeO)_2$-4-pyrimidinyl	167-9
244	-	COOMe	Me	2-Ph-5-pyrimidinyl	gum
245	-	COOMe	H	2,6-Cl_2-5-pyrimidinyl	135-7
246	-	COOMe	H	2-NC-5-pyrimidinyl	186-8
247	-	COOMe	H	4,5-$(MeO)_2$-2-pyrimidinyl	182-3

Cpd	$(R^1)_n$	Z	Y	A	m.p.(°)
248	-	COOMe	H	4,6-$(MeO)_2$-2-pyrimidinyl	163-4
249	-	COOMe	H	2-MeONH-5-pyrimidinyl	194-6
250	-	COOMe	H	2-MeNH-5-pyrimidinyl	230-1
251	-	COOMe	H	2-Cl-4-(2-MeOCO-PhNH)-5-pyrimidinyl	190-2
252	-	COOMe	H	5-Cl-6-Me-2-pyrazinyl	136-41
253	-	COOMe	H	5-MeO-6-Me-2-pyrazinyl	166-9
254	-	COOMe	H	2-(N-methoxy-N-methoxycarbonyl-amino)-5-pyrimidinyl	151-2
255	-	COOMe	H	2-cyclopropyl 5-pyrimidinyl	112-4
256	3-MeOCO	COOMe	H	6-MeO-3-pyridyl	111-4
257	-	COOMe	H	2-MeS-5-pyrimidinyl	160-2
258	-	COOMe	H	5,6-Cl_2-2-pyrazinyl	143-8
259	-	COOMe	H	5-(2-thienyl)-3-pyridyl	148-9
260	-	COOMe	H	5-(4-CF_3-Ph)-3-pyridyl	155-6
261	-	COOMe	H	5-($ClSO_2$)-3-pyridyl	144-5
262	-	COOMe	H	5-(Cl_2CHS)-3-pyridyl	120-2
263	-	COOMe	H	5-(NH_2SO_2)-3-pyridyl	185-7
264	-	COOMe	H	5-Br-6-Cl-3-pyridyl	157-9
265	-	COOMe	Me	5-NO_2-6-MeO-3-pyridyl	98-100

Cpd	$(R^1)_n$	Z	Y	A	m.p.(°)
266	-	COOMe	H	2-(1-imidazolyl)-5-pyrimidinyl	193-5
267	-	COOMe	H	4-MeO-2-MeS-5-pyrimidinyl	140-2
268	-	COOMe	Me	2,6-$(MeO)_2$-4-pyrimidinyl	101-3
269	-	COOH	3,4-$(MeO)_2$-benzyl	6-MeO-3-pyridyl	123-4
270	-	COOMe	H	5-(Me_2NSO_2)-3-pyridyl	169-70
271	-	COOMe	H	5-Br-6-MeO-3-pyridyl	169-70
272	-	COOMe	H	5-Br-6-$MeSO_2$-3-pyridyl	223-5
273	-	COOMe	H	5-Br-6-MeSO-3-pyridyl	160-2
274	-	$COOC_5H_{11}$	H	2-MeO-3-pyridyl	47-8
275	-	COO-allyl	H	2-MeO-3-pyridyl	80-1
276	-	COOMe	2-Me-benzyl	6-(2-Me-benzyl)-3-pyridyl	oil
277	-	COOMe	H	2-Cl-4-quinolinyl	163-4
278	-	COOMe	$-CH_2Ph$	6-MeO-3-pyridyl	101-2
279	4,5-MeO_2	COOMe	H	2-MeO-3-pyridyl	152-4
280	-	COOMe	H	5-NH_2-6-MeO-3-pyridyl	202-3
281	-	COOMe	Me	2,4-$(MeO)_2$-5-pyrimidinyl	78-81
282	-	COOMe	2-MeO-benzyl	2-MeO-5-pyrimidinyl	gum
283	-	COOMe	H	4-Me-2-MeS-5-pyrimidinyl	78-81

Cpd	$(R^1)_n$	Z	Y	A	m.p.(°)
284	-	COOMe	H	2-(3-pyridyloxy)-5-pyrimidinyl	124-6
285	-	COOMe	H	2-F-3-pyridyl	130-1
286	-	COOMe	2-Me-benzyl	$5,6-(MeO)_2$-3-pyridyl	oil
287	-	COOMe	H	5,6-methylenedioxy-3-pyridyl	168-79
288	-	COOMe	H	5-I-6-MeO-pyridyl	173-5
289	$3,4-Me_2$	COOMe	H	2-MeO-3-pyridyl	126-7
290	4-Cl	COOMe	H	2-MeO-3-pyridyl	128-30

The following compounds were also prepared

a) ethyl N-(6-methoxy-3-pyridinethiocarbonyl)anthranilate, as an oil, (compound 291)

b) methyl N-(5,6-dimethoxy-3-pyridinethiocarbonyl)-anthranilate, m.p. 154-5°, (compound 292)

c) methyl N-(2-methoxy-5-pyrimidinethiocarbonyl)-anthranilate, m.p. 135-7°, (compound 293), and

d) isobutyl N-(6-methoxy-3-pyridinethiocarbonyl)-anthranilate, as an oil, (compound 294).

Test Example

Compounds are assessed for activity against one or more of the following:

Phytophthora infestans: late tomato blight
Plasmopara viticola: vine downy mildew
Erysiphe graminis: barley powdery mildew
Pyricularia oryzae: rice blast
Pellicularia sasakii: rice sheath blight
Botrytis cinerea: grey mould
Venturia inaequalis: apple scab
Leptosphaeria nodorum: glume blotch

Aqueous solutions or dispersions of the compounds at the desired concentration, including a wetting agent, were applied by spray or by drenching the stem base of the test plants, as appropriate. Plants or plant parts were then inoculated with appropriate test pathogens and kept under controlled environment conditions suitable for maintaining plant growth and development of the disease. After an appropriate time, the degree of infection of the affected part of the plant was visually estimated. Compounds were considered active if they gave greater than 50% control of the disease at a concentration of 500 ppm (w/v) or less.

Compounds 30, 36, 43, 47, 58, 112, 115, 180, 242 and 286 showed activity against *Phytophthora infestans*;
Compounds 9, 30, 36, 40, 42, 57, 58, 59, 62, 64, 67-70, 76, 77, 82, 83, 96, 112, 115, 127, 129, 130, 132, 138, 139, 161, 163, 166, 181, 186, 200-204, 210, 213, 234, 248, 249, 261, 267, 266, 268, 271 and 277 showed activity against *Plasmopara viticola*;
Compounds 1-3, 9-12, 20, 23, 25, 27- 29, 32, 33, 34, 38, 39, 41, 46, 50, 52, 62, 66, 70, 73, 83, 84, 90, 91, 104-108, 110, 113, 115, 121-123, 132, 135, 145, 154, 155, 163, 176, 177, 196, 200, 208, 209, 210-2, 213, 218, 228, 239, 243, 249, 250, 252-4, 258, 265, 268, 271-3, 275, 276, 278 and 286 showed activity against *Erysiphe graminis*;

Compounds 1, 1a, 2, 6a, 48, 49, 54-56, 65, 68, 72, 74, 75, 126, 129, 145, 146, 169, 171, 197, 230, 232, 249, and 277 showed activity against *Pyricularia oryzae*;

Compounds 14, 44, 49, 62, 114, 115, 152, 211, 215, 216 and 278 showed activity against *Pellicularia sasakii*;

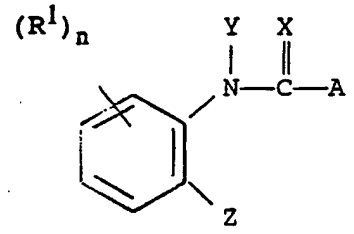
Compounds 48, 51, 52, 53, 61, 63, 121, 129, 195, 228 and 251 showed activity against *Botrytis cinerea*;

Compounds 1, 8, 12, 17, 45, 63, 86, 104, 112, 119, 146, 149, 150, 151, 187, 189, 204, 211, 219, 224, 239, 244, 245, 248 and 250 showed activity against *Venturia inaequalis*; and

Compounds 24, 35, 60, 61, 71, 204, 216, 220 and 249 showed activity against *Leptosphaeria nodorum*.

CLAIMS

1. A compound of formula I



(I)

X is O or S;

A is a 6 membered heteroaryl group comprising at least one nitrogen atom, which is optionally substituted by one or more of the group R^2;

R^1 is alkyl, cycloalkyl, cycloalkenyl, alkenyl, alkynyl or amino, (each of which is optionally substituted), Y^1-X-, halogen, cyano, nitro, acyl, acyloxy, optionally substituted heterocyclyl or optionally substituted phenyl; or two adjacent groups together with the carbon atoms to which they are attached can form an optionally substituted benzo ring;

R^2 has the same meaning as R^1 or two adjacent groups together with the carbon atoms to which they are attached can form an optionally substituted heterocyclic ring;

Y is alkyl, cycloalkyl, cycloalkenyl, alkenyl or alkynyl, each of which is optionally substituted, hydrogen or acyl;

Y^1 has the same meaning as Y or is optionally substituted phenyl or optionally substituted heterocyclyl;

Z is $C(=X^1)-X^2-R^3$, cyano, nitro, amino, acyl, optionally substituted heterocyclyl, $-C(R^5)=N-OR^6$ or $-C(R^5)=N-NR^6R^7$;

R^3 is alkyl, cycloalkyl, cycloalkenyl, alkenyl, alkynyl, phenyl or heterocyclyl, each of which is optionally substituted, hydrogen or an inorganic or organic

cationic group;

X^1 and X^2, which may be the same or different, are O or S;

R^5, R^6 and R^7, which may be the same or different, are alkyl, cycloalkyl, cycloalkenyl, alkenyl, alkynyl, phenyl or heterocyclyl, each of which is optionally substituted or hydrogen or R^6 and R^7 together with the atom(s) to which they are attached can form a ring;

and n is 0 to 4,

together with complexes with metal salts, as well as salts with bases of compounds which are acids and salts with acids of compounds which are bases, with the proviso that when Y is hydrogen and

i) when Z is carboxy, methoxycarbonyl or ethoxycarbonyl ring A is not unsubstituted pyridyl or pyrazinyl; and

ii) when Z is carboxy and n is 0, A is not 2-chloro-3-pyridyl, 6-(2-diethylaminoethoxy)-3-pyridyl or a 2-pyridyl group.

2. Fungicidal compositions which comprise a compound as claimed in claim 1 in admixture with an agriculturally acceptable diluent or carrier.

3. A method of combating phytopathogenic fungi at a locus infested or liable to be infested therewith, which comprises applying to the locus a compound as claimed in claim 1.

INTERNATIONAL SEARCH REPORT

Intern al Application No
PCT/GB 95/00570

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C07D213/82 C07D213/81 C07D239/30 C07D215/50 C07D241/24
C07D401/12 C07D409/04 A01N43/40 C07D413/12 C07D405/12
C07D417/12 C07D413/04 C07D401/04

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C07D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	AGRICULTURAL AND BIOLOGICAL CHEMISTRY, vol. 44,no. 9, 1980 TOKYO JP, pages 2143-2147, O. KIRINO ET AL. 'Fungicidal activity of N-benzoylanthranilates and related compounds' see table II	1-3
X	DE,A,24 17 216 (BASF AG) 6 November 1975 see the whole document	1-3

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
2 May 1995	15. 05. 95

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax (+31-70) 340-3016	Bosma, P

Form PCT/ISA/210 (second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

International application No.
PCT/GB95/00570

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

A complete search is not possible on economic grounds, because the subject matter of claim 1 is too broad and comprises many already known compounds. Therefore the search has been based on the examples and the claims as indicated below. (Claim 1 has been searched incompletely)

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. ☐ As all searchable claims could be searches without effort justifying an additional fee, this Authority did not invite payment of any additional fee.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest.

☐ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

Inter nal Application No
PCT/GB 95/00570

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
DE-A-2417216	06-11-75	AT-B-	341828	27-02-78
		BE-A-	827567	06-10-75
		CA-A-	1030446	02-05-78
		CH-A-	594353	13-01-78
		FR-A,B	2267043	07-11-75
		GB-A-	1494695	14-12-77
		NL-A-	7504178	13-10-75
		US-A-	4001416	04-01-77